COATINGS

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PROTECTIVE-DECORATIVE COATINGS FOR CONSTRUCTION CERAMICS BASED ON WEST SIBERIAN NATURAL RAW MATERIAL

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The results of using wollastonite rocks in engobe coating compositions for finishing construction ceramics with improved decorative and performance properties in comparison to existing analogs are reported; this allows expanding the raw material base of enterprises in the domestic construction materials industry.

Construction materials made of traditional ceramic materials are not always resistant to environmental factors. In exposure to temperature and aggressive gases, their physicochemical properties irreversibly change and as a consequence, they gradually deteriorate, losing their external esthetic appearance. One method of prolonging the lifetime of construction ceramics is to apply surface protective-decorative coatings; engobes are such coatings.

Strong adhesion of the face layer with the ceramic base, uniform thickness and color are the basic requirements for decorated construction ceramics. The degree of adhesion of the coating to the article is a function of optimum selection of their compositions based on air and firing shrinkage indexes, which should be close — a maximum difference of 1 – 1.5% (the version where the total shrinkage of the engobe layer is 0.5 – 0.7% higher than the overall shrinkage of the basic mass is best) and the correspondence of their TCLE: the difference between them should not be greater than 8 – 10%.

Incorporation of different additives in the engobe allows correcting its properties (RF Patent No. 2052434) [1, 2] and the combining ability with the ceramic base. However, in many cases, it is not always possible to ensure the required strength of adhesion of the coating with the ceramic matrix, which limits the lifetime of engobed articles in real conditions.

Two varieties of raw materials — clay and nonplastic — are traditionally used in engobe coatings. Quartz sand, cullet, etc., are usually used as the nonplastic components (RF Patent No. 2257364). We used wollastonite rock as the nonplastic additive, selected because of the needle shape of the crystals in the rock-forming mineral (wollastonite), which allows predicting the potentially possible good covering power of the coating and reliable adhesion of the coating with the ceramic base of the article.

Wollastonite rock from the Sinyukhinskoe deposit in the Altai Krai was used for the study in the form of finely milled polydisperse white powder of the following granulometric composition: 10% 160 – 100 μm, 32% 100 – 60 μm, 43% 60 – 20 μm, 15% less than 20 μm.[2]

Evaluation of the wollastonite rock with respect to the chemical (Table 1) and mineral compositions showed that it

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[2] Here and below: mass content.

TABLE 1

Raw material component	Mass content, %							
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	calcination loss
Wollastonite rock	47.11	1.04	1.01	4.97	44.09	0.23	0.17	1.38
Voronovskoe clay	56.34	26.61	1.66	1.36	0.75	1.64	1.75	9.89

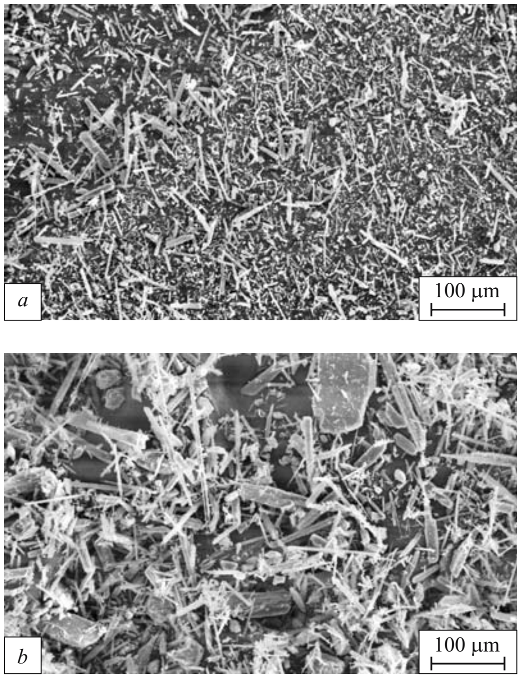

Fig. 1. Electron microscopic photographs of wollastonite rock in the initial state (a, × 500) and fired at 1000°C (b, × 800).

is wollastonite–diopside raw material (64.8% wollastonite and 26.6% diopside) with insignificant impurities of quartz (3.8%), calcite (3.5%), and magnesite (1.3%).

A comparison of the diffractograms of raw rocks and rocks fired at 1000°C indicates their identity, except for the disappearance of the reflection of calcite due to its dissociation. Three types of particles are seen in the electron micrographs of the unfired sample (Fig. 1*a*): needle-shaped particles of wollastonite with a needle length of 20 – 200 μm and thickness of 2 – 10 μm, particles of prismatic (bar-shaped) habit 50 – 100 μm long and 10 – 50 μm thick, which were undersplit during mechanical preparation of the bench rock (aggregates) from needle-like particles of wollastonite, and particles with a smaller length and width ratio due to the presence of impurity minerals.

Firing wollastonite rock (Fig. 1*b*) at 1000°C did not change the crystal habit, which demonstrates the thermal stability of wollastonite on heating to 1000°C. This composition and structure of wollastonite rock particles make it possible to use it as a structure-forming component for fabricating high-strength ceramic materials and for special ceramic coatings.

TABLE 2

Wollastonite rock content	Total shrinkage, %		Water absorption, %		Compressive strength, MPa	
	1000°C	1050°C	1000°C	1050°C	1000°C	1050°C
0	6.6	8.8	16.9	13.0	21.7	25.2
20	5.8	6.4	14.8	10.9	30.2	39.1
30	4.6	6.1	14.5	10.0	31.6	53.1
40	4.5	5.0	15.9	12.3	29.8	42.0
50	4.4	3.9	16.1	14.0	25.4	36.9

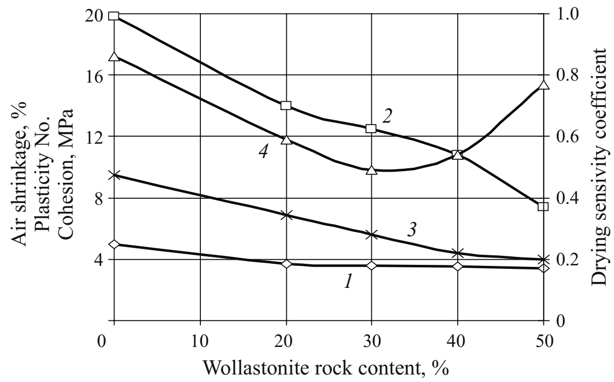

Fig. 2. Effect of addition of wollastonite rock on the process properties of Voronovsk clay: *1*) air shrinkage; *2*) plasticity number; *3*) cohesion; *4*) drying sensitivity coefficient.

In developing the engobe coatings, white-burning clay from the Voronovskoe deposit (Tomsk region) was used as the plastic material in developing the engobe coatings. The amount of wollastonite rock added was varied from 20 to 50% with a step of 10%. The samples were prepared by plastic molding.

It was found that incorporation of up to 50% wollastonite rock continuously decreased the air shrinkage and plasticity of the experimental pastes (Fig. 2). The optimum content of wollastonite rock that ensures the greatest cohesion of the ceramic pastes is determined by the nature of the clay raw material. Voronovsk clay permits addition of up to 30% insert additive without worsening the strength of the samples in an air-dried state. Increasing the content of finely disperse wollastonite rock above 30% is accompanied by an increase in the sensitivity to drying and a decrease in the crack resistance of the articles.

After drying to the air-dried state, the samples were fired at 1000 and 1050°C with holding at the final temperature for 1 h. The ceramic properties of the samples of clay–wollastonite pastes are reported in Table 2.

Since water absorption of the samples of engobe pastes analyzed is significantly higher than the requirements (10 – 15% versus 1 – 3%) and sintering of the clay–wollastonite compositions must be activated by adding a low-melting component, colorless electric lamp glass cullet in the amount of 5 – 30% was used as the component. The three-component compositions of the engobe pastes are reported in Table 3.

Preparation of the raw materials, pastes, and samples, and the heat-treatment conditions were the same as in the preceding series of experiments.

It was found that pastes V10, V11, and V12 containing 20 – 25% wollastonite rock, 20 – 30% cullet, and the re-

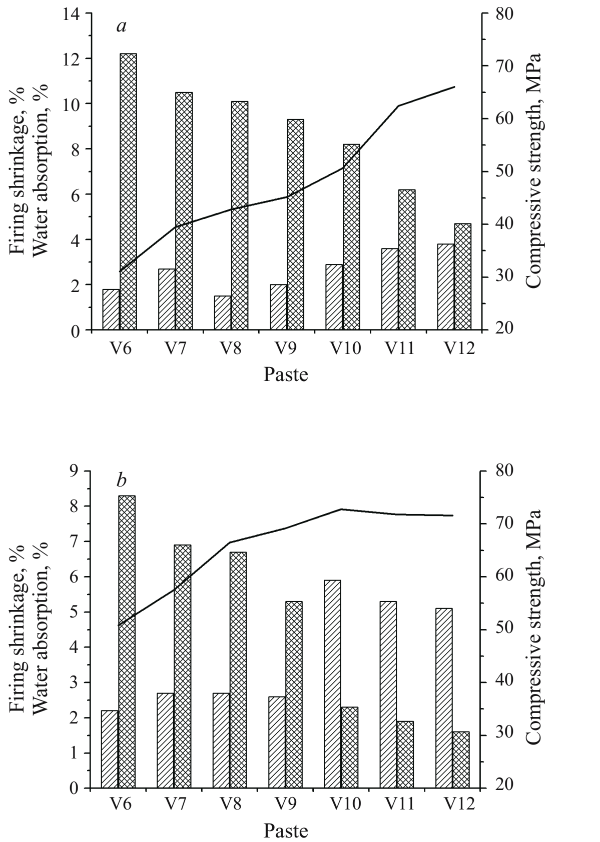

Fig. 3. Histogram of the change in the ceramic properties of samples of three-component engobe pastes fired at 100°C (*a*) and 1050°C (*b*):) shrinkage, %;) water absorption, %; ——) strength, MPa.

mainder, clay, are promising compositions that satisfy the requirements for engobes with respect to the degree of sintering (Fig. 3).

The x-ray diffractograms of samples of the recommended engobe pastes fired at 1050°C are characterized only by intensive reflections characteristic of wollastonite from the wollastonite rock and residual quartz and cristobalite as a product of partial degeneration of quartz added with the clay.

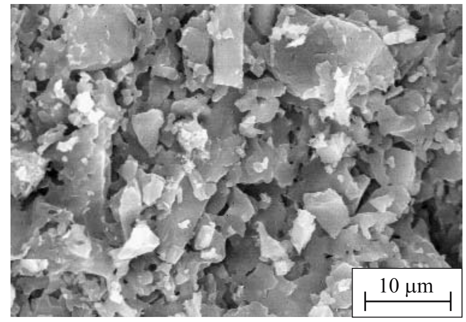

Fig. 4. Electron microscopic photographs of engobe coating with wollastonite concentrate in glass cullet fired at 1000°C (× 2400).

Elongated particles of wollastonite are clearly seen in the photomicrographs of the engobe coating (Fig. 4).

Practical engobe compositions based on white-burning clays using wollastonite rock as the structure-forming component and colorless glass cullet that plays the role of flux were developed as a result of the studies (RF Patent No. 2257364). The engobe was prepared by the slip method by combined milling of all components in a ball mill to 1.0 – 1.5% residue in a No. 0063 sieve and a slip moisture content of 40 – 45%.

Engobe slip with a density of 1.52 – 1.58 g/cm^3 and fluidity (after 30 sec) of 10 – 12 sec (6 mm viscometer hole diameter) was applied by pouring or spraying on the faces of dried semifinished product and fired ceramic brick. The engobed samples were dried to a coating moisture content of 2 – 3% and then fired at a temperature of 1020 – 1050°C.

The needle shape of the wollastonite crystals ensures the good covering power of the engobe coating and combined with glass cullet, good adhesive strength. Blocking of open pores on the face of the article due to application of the densely sintered engobe layer, which decreases the overall moisture saturation of the article during service in construction structures, and when the strength of adhesion of the decorative layer to the ceramic base is sufficient, the cold resistance of the decorated facing ceramics does not decrease (Table 4).

TABLE 3

Paste	Mass content, %		
	binder component (clay)	structure-forming component (wollastonite)	flux (cullet)
V6	65	30	5
V7	60	30	10
V8	65	25	10
V9	60	25	15
V10	55	25	20
V11	50	25	25
V12	50	20	30

TABLE 4

Sample*	TCLE,** 10^{-6} K^{-1}	Shrinkage, %	
		air	firing
Ceramic base	6.4	3.0	4.7
Engobe paste:			
V10	5.6	2.8	5.3
V11	6.3	2.7	5.8
V12	5.9	2.7	4.7
Engobed article	–	3.0	4.8

* The cold resistance was 50 cycles in all cases.

** In the 20 – 800°C temperature range.

TABLE 5

Engobe coating	Engobe tensile strength, MPa,* in application on	
	dried semiproduct	fired article
V10	> 3.11	> 5.07
V11	> 3.04	> 4.39
V12	> 2.85	> 4.26

* The tensile strength values are reported with the "greater than" symbol since the coating ruptured along the brick.

The strength of adhesion of the engobe to the ceramic base after baking at 1020 – 1050°C was determined to estimate the lifetime of the engobe coating (Table 5).

Composites of the following composition (%) are thus recommended as engobe coatings: 30% clay, 25% wollastonite rock, 45% glass cullet.

Sufficient chemical purity of the wollastonite rock and use of transparent glass cullet (with a maximum coloring oxide content of 0.2%) increase the whiteness of the coating and improve the decorative properties of the engobed article. The required color palette of the coating is determined by selecting the ceramic pigment, added in the amount of 1 – 10% (above 100%).

The proposed engobe compositions were tested in conditions of a working face ceramic brick plant.

In addition to using them directly as engobes, the developed coatings are also recommended as an intermediate layer that masks the color of the ceramic base, with subsequent application of low-melting transparent glazes, which eliminates the use of expensive opaque glazes in production of glazed facing ceramics.

REFERENCES

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2. I. A. Al'perovich and V. G. Bekrenev, "Increasing the lifetime of bilayer facing brick with a wide color palette," *Stroit. Mater.*, No. 7, 9 – 12 (1994).